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Quantitative risk assessment for accidental release of titanium tetrachloride in a titanium sponge production plant

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Abstract

This paper outlines the quantitative risk assessment for storage and purification section of a titanium sponge production facility. Based on qualitative HAZAN technique, which involves a detailed FETI and HAZOP study of the entire plant, the storage and the purification section were found to be the most hazardous sections. Titanium tetrachloride ($TiCl_4$) is the major reactant used in this plant. $TiCl_4$ is a toxic, corrosive water reactive chemical and on spillage from containment creates a liquid pool that can either boil or evaporate leading to the evolution of toxic hydrogen chloride (HCl). Fault tree analysis technique has been used to identify the basic events responsible for the top event occurrence and calculate their probabilities. Consequence analysis of the probable scenarios has been carried out and the risk has been estimated in terms of fatality and injuries. These results form the basic inputs for the risk management decisions.

Keywords: Risk analysis; Hazard assessment; Fault tree analysis; Consequence analysis; Titanium tetrachloride

1. Introduction

The need for risk assessment of process plants has become exceedingly critical due to the trend towards larger and more complex units that process toxic, flammable or otherwise hazardous chemicals under extreme temperature and pressure conditions. Moreover, the potential damage has been magnified by the proximity of many such operations to densely populated areas. Increasing public awareness of technological risks has placed a greater responsibility on the process industries to review and revise their current safety practices to make the process technologies both intrinsically and extrinsically safer. Risk and hazard

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analysis is a tool whereby potential hazards to plant personnel and surrounding public are defined and associated risks are computed based on the likelihood and consequence level.

This paper presents the quantitative risk assessment study carried out for a titanium sponge experimental facility set up for establishing technology for titanium production in large commercial size batches. The plant involves storage and purification of $TiCl_4$, which is an aggressive water reactive chemical mainly because of its pronounced halo anhydride character [1–7]. The hazardous nature of this substance is recognised in various items of legislation relating to industrial safety. Under the new Seveso II EU Directive, all substances that attract risk phrase R 14 'reacts violently with water' (including R14/15-minimum quantity 100 T) or R29 'in contact with water, liberates a toxic gas' (minimum quantity 50 T) are described as major hazards and are included in the list of chemicals covered by the directive [8], which was implemented in the UK as the COMAH regulations in 1999 [9]. EPA's Office of Air Quality Planning and Standards also considers titanium tetrachloride to be a "high concern" pollutant [10–13] based on its severe toxicity.

A recent survey of accidents that occurred in USA between January 1990 and November 1999 revealed that there have been 473 incidents involving spillage of $TiCl_4$ alone, out of which 13 involved evacuation, injuries or deaths [14–17]. Even so, there are almost no experimental data on the behaviour of this chemical on release. A recent accident in 2001 involved leakage of titanium chloride from a tanker. Although the liquid involved was as little as a few hundred millilitres, it was enough to generate a considerable volume of hydrogen chloride which not only affected the employees working there but also the staff of the neighbouring premises as the resultant escaping gas drifted towards them [18]. This clearly indicates the extent of hazard involved in handling this chemical. This paper aims at quantifying these hazards and their consequences by using well-known techniques of fault tree and consequence analysis and estimating the risk to surrounding population. We have also attempted to model the behaviour of the $TiCl_4$ pool, which is formed in case of spillage. It is to be noted that this requires validation data, but the availability of such data awaits the performance of suitable experimental investigations.

1.1. Process description

A demonstration plant has been set up for establishing the technology of production of titanium sponge in large commercial size batches. The process adopted here is high temperature reduction of $TiCl_4$ by molten magnesium followed by pyrovacuum distillation leading to the formation of titanium sponge. The plant consists of the following sections:

- $TiCl_4$ storage and purification section;
- metal production bay;
- sponge ejection bay and sponge crushing bay.

The storage section comprises of 25T capacity horizontally placed SS 304L tanks mounted on a concrete floor. $TiCl_4$ is transferred to the adjacent sections and standby tanks through

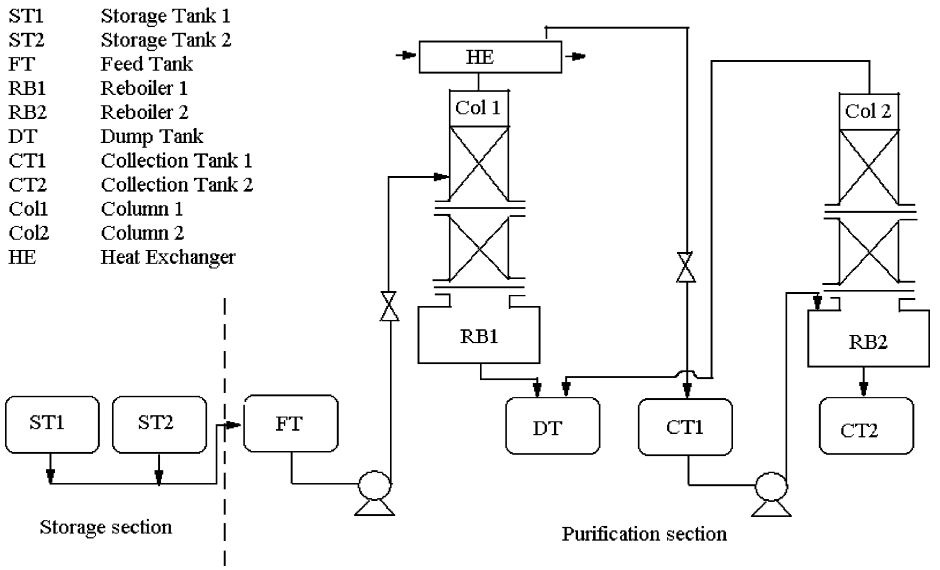


Fig. 1. Process flow sheet for $TiCl_4$ storage and purification.

pipelines. The purification involves two-stage distillation of as-received $TiCl_4$ for removal of dissolved gases, volatile compounds such as $SiCl_4$, $SnCl_4$, etc. and dissolved solids such as $TiOCl_2$. The flow sheet for the process described is shown in Fig. 1. Ten tons of untreated $TiCl_4$ is fed into the feed tank and the distillation is started by running both columns (Col. 1 and Col. 2). In the stripping column (Col. 2), overflow is avoided to prevent any bottom draw. The level in Col. 2 is maintained by matching the feed rate of the liquid with the vapour rate. The pure chloride is collected in collection tank I. The distillation is stopped when the liquid in feed tank is emptied. The material in both the reboilers is dumped into dump tank. After drainage is completed, reboiler-2 is filled up with the material from collection tank I. The distillation is performed only in the second column by recycling the once-distilled chloride from collection tank I. The double distilled chloride is collected in collection tank II, which is used as the feed for the reduction process in the subsequent metal production section.

1.2. Hazard identification

Fire explosion and toxicity index (FETI) analysis and hazard and operability (HAZOP) studies have been used to identify the hazardous sections of the plant. Both the storage as well as the purification sections have been categorised as “medium toxicity” hazard and “low fire and explosion” hazard on the basis of FETI analysis. In addition to this, the inventory of the material in the storage section is large, so it has been taken up for detailed qualitative and quantitative assessment. The major hazards identified from HAZOP studies are the “release of hydrogen chloride (HCl) due to spillage/leakage caused by rupture of $TiCl_4$ storage tanks” and the “rupture of heat exchanger (HE) leading to HCl evolution”.

Both probabilistic analysis and consequence analysis has been carried out for the resulting scenarios.

1.3. Fault tree analysis

Fault tree analysis technique has been used for probabilistic analysis. The fault tree analysis gives all possible minimum combinations of basic human, instrument and equipment failures called minimum cut sets, which could lead to the occurrence of the critical event, commonly known as the ‘top event’. The fault tree is solved to obtain the set of basic events whose combination would lead to the occurrence of the unwanted top event.

1.3.1. Release of HCl due to spillage/leakage caused by rupture of storage tank

The fault trees for the top events are shown in Fig. 2(a)–(f). The failure rates of the events are based on the data from several sources [19,20], suitably modified, where necessary to account for Indian conditions.

The total number of minimal cut sets for this fault tree has been computed to be 1566. The minimal cut sets in order of increasing number of years or decreasing number of occurrence of top event are listed in Table 1.

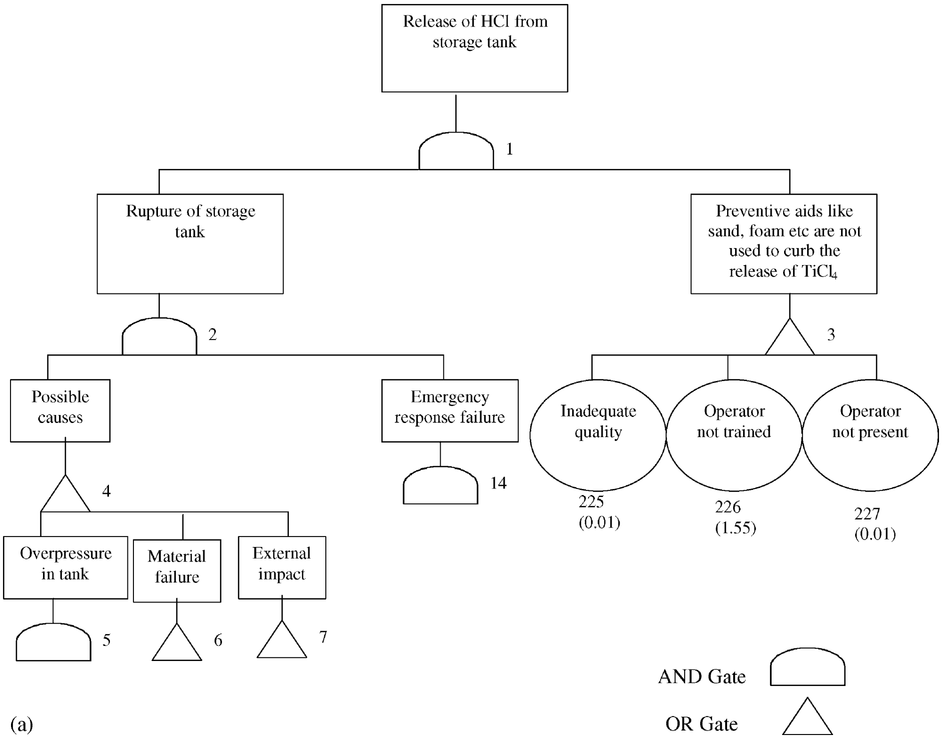


Fig. 2. Fault tree for release of HCl from storage tank.

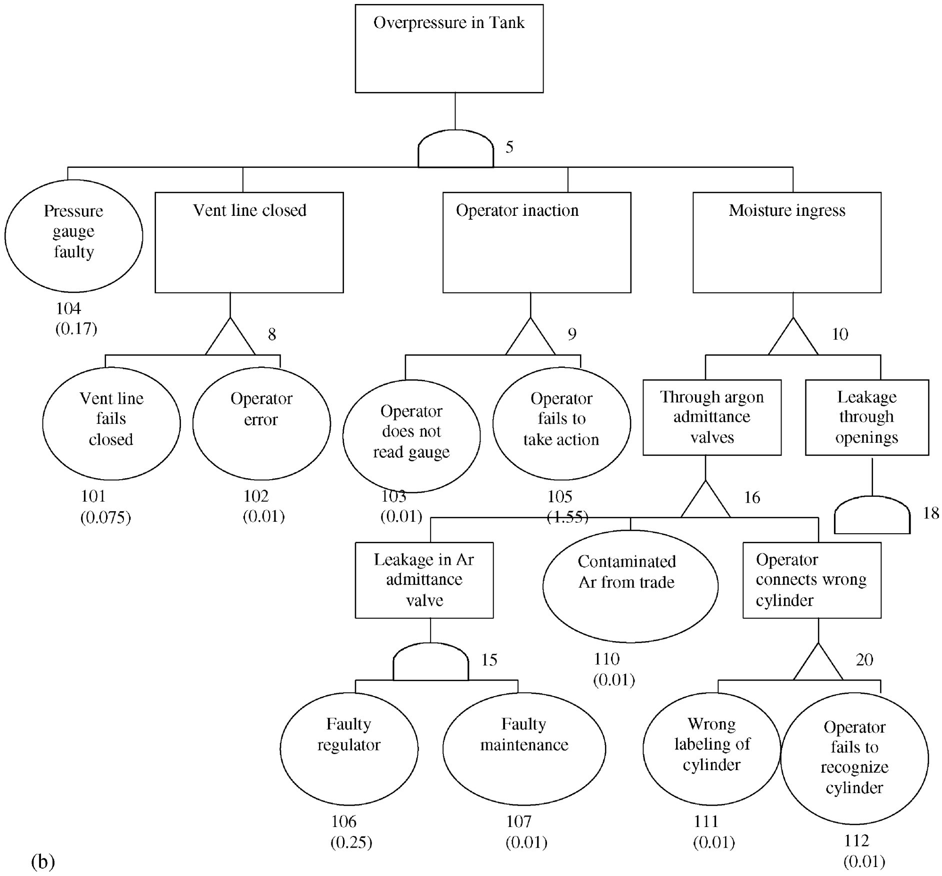
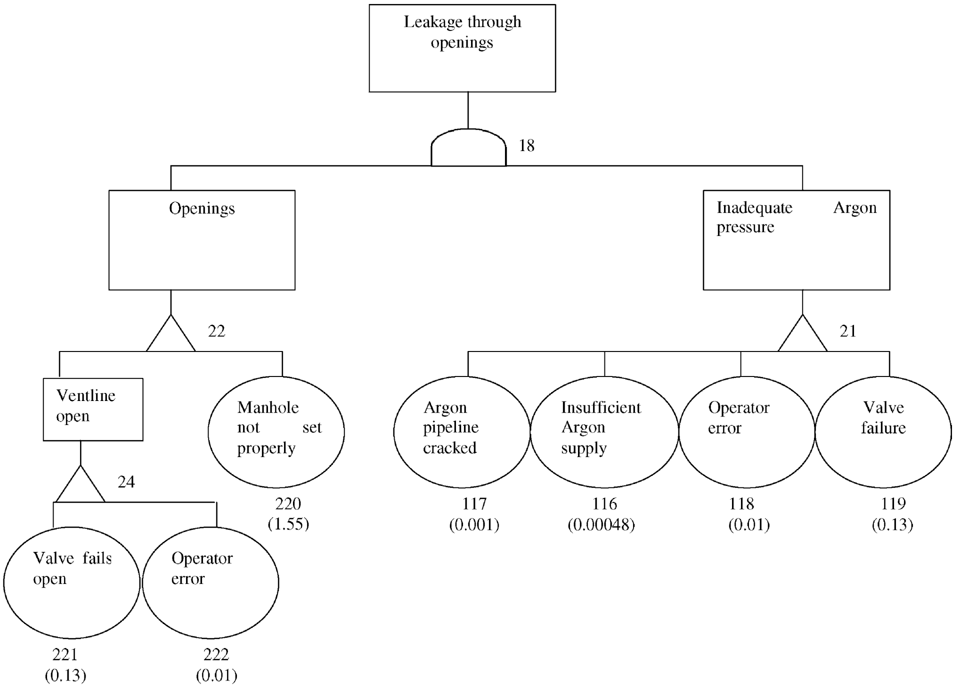


Fig. 2. (*Continued*)

Table 1
Fault tree analysis of top event occurrence "release of HCl due to rupture of storage tank"

	Minimal cut sets	Failure rates (faults per year)	Years between two faults
1	(119)(220)(230)(231)(234)(229)(226)	2.3E−02	4.2E+01
2	(110)(230)(231)(234)(229)(226)	2.4E−03	4.1E+02
3	(111)(230)(231)(234)(229)(226)	2.4E−03	4.1E+02
4	(112)(230)(231)(234)(229)(226)	2.4E−03	4.1E+02
5	(113)(230)(231)(234)(229)(226)	2.4E−03	4.1E+02
6	(118)(220)(230)(231)(234)(229)(226)	1.9E−03	5.2E+02
7	(106)(107)(230)(231)(234)(229)(226)	5.3E−04	1.8E+03
8	(101)(104)(119)(220)(231)(234)(229)(226)(105)	3.6E−04	2.7E+03
9	(119)(220)(230)(231)(233)(229)(226)	3.6E−04	2.9E+03
10	(119)(220)(230)(231)(234)(228)(226)	2.9E−04	3.3E+03



(c)

Fig. 2. (*Continued*)

Operator errors in tackling with the release and electricity failure were identified as the basic failures which result in high frequency of top event occurrence. The failure rate of the top event has been calculated to be 2.3E−02. Previous studies [21,22] reveal that operator related failures are generally more common than instrument failures and due to their unpredictability, the complexity of the situation increases manifold.

1.3.2. *Rupture of HE*

The total number of minimal cut sets for the tree "rupture of HE" has been computed to be 12. The fault trees for the top event are shown in Fig. 3(a)–(d). The minimal cut sets in order of increasing number of years or decreasing number of occurrence of top event are listed in Table 2. Maintenance of upstream conditions and operator error in monitoring temperature were identified as the basic failures which result in high frequency of top event occurrence. The failure rate of the top event has been calculated to be 1.33E−02.

On the basis of the observations, brought forward by fault tree analysis, recommendations regarding maintenance/operators training have been suggested.

1.4. *Sensitivity analysis*

Sensitivity analysis has been carried out to determine the effect of incorporating the suggested modifications on system safety. The results of the analysis are shown in Table 3.

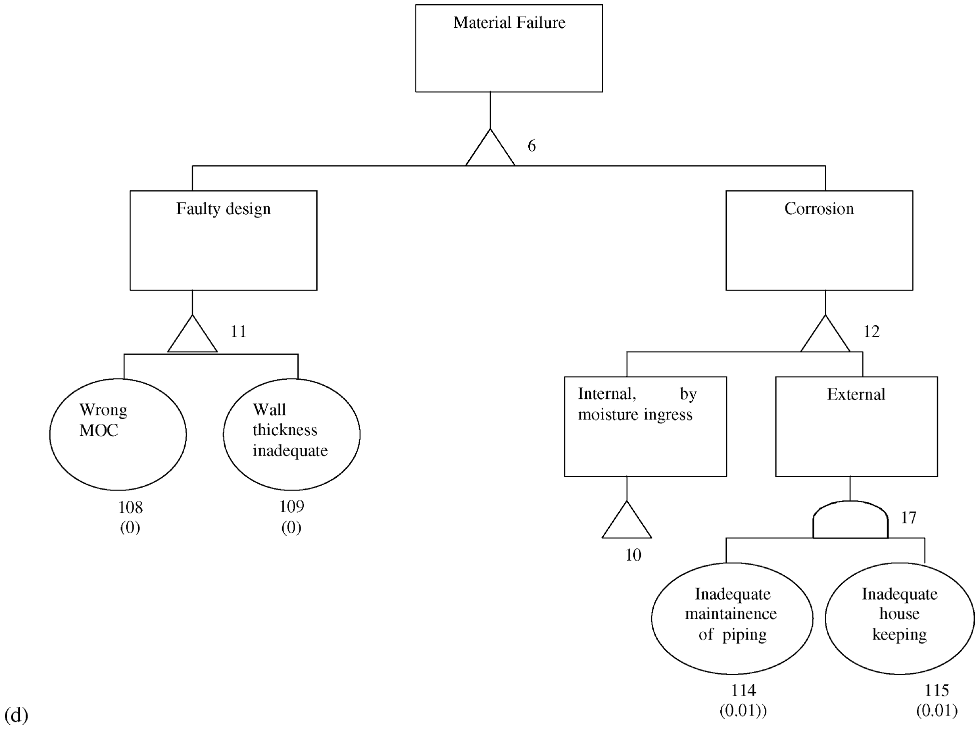


Fig. 2. (*Continued*)

It is apparent that incorporation of the suggested modifications in the form of two separate actions (i.e. use of generator and operator training) can bring down the top event probability from 2.3E−02 to 1.06E−06 thereby causing improvement of several orders of magnitude in system safety.

Table 2
Fault tree analysis of top event occurrence "rupture of HE"

	Minimal cut sets	Failure rates (faults per year)	Years between two faults
1	(112)(114)	1.3E−02	7.5E+01
2	(104)(116)	8.6E−04	1.2E+03
3	(101)(103)	8.6E−04	1.2E+03
4	(112)(113)	8.6E−04	1.2E+03
5	(101)(102)	5.6E−05	1.7E+04
6	(104)(115)	5.6E−05	1.7E+04
7	(109)(118)(110)	5.2E−09	1.9E+08
8	(109)(118)(111)	5.2E−09	1.9E+08
9	(109)(117)(110)	3.36E−10	2.9E+09
10	(109)(117)(111)	3.36E−10	2.9E+09

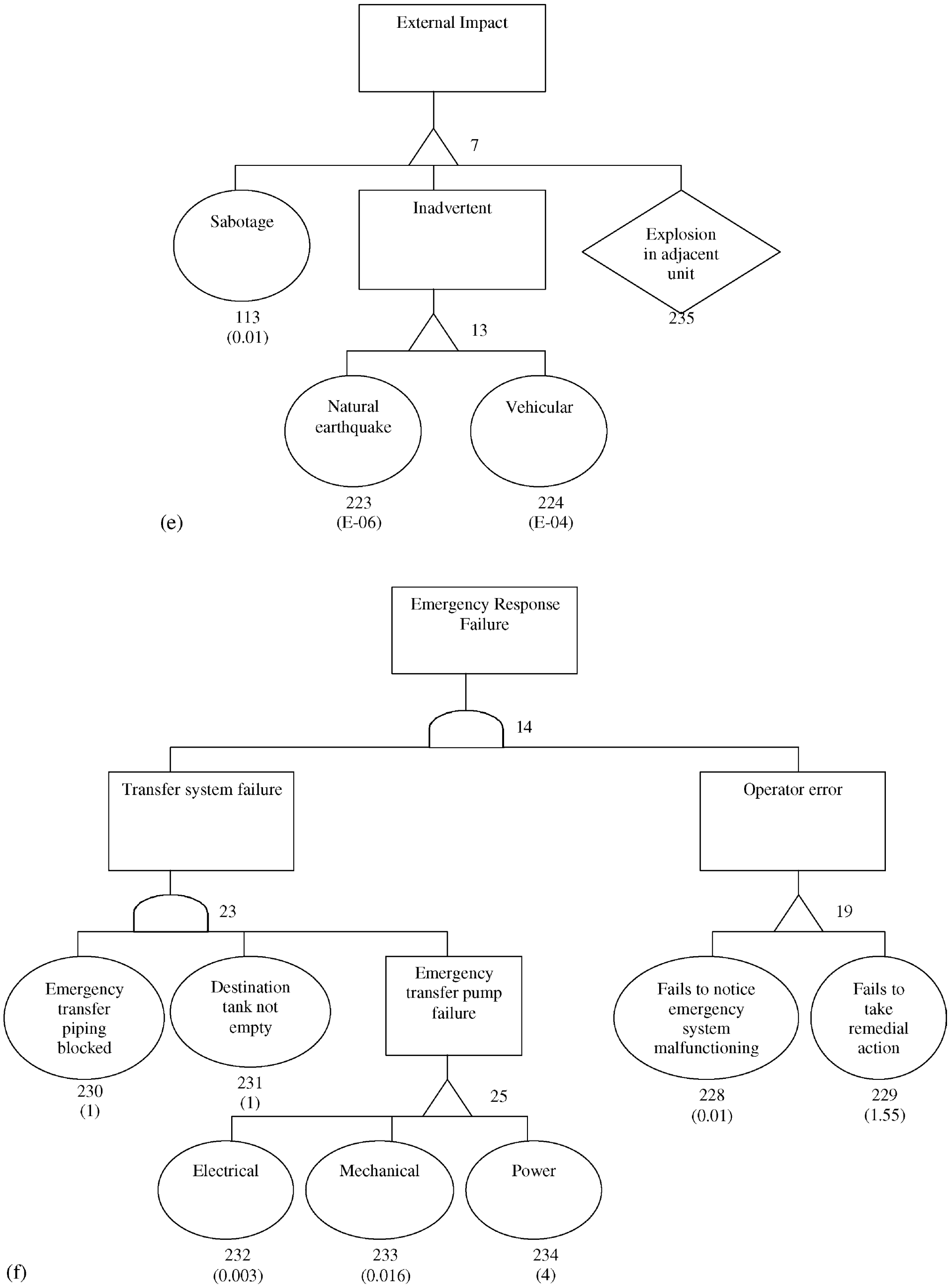


Fig. 2. (*Continued*).

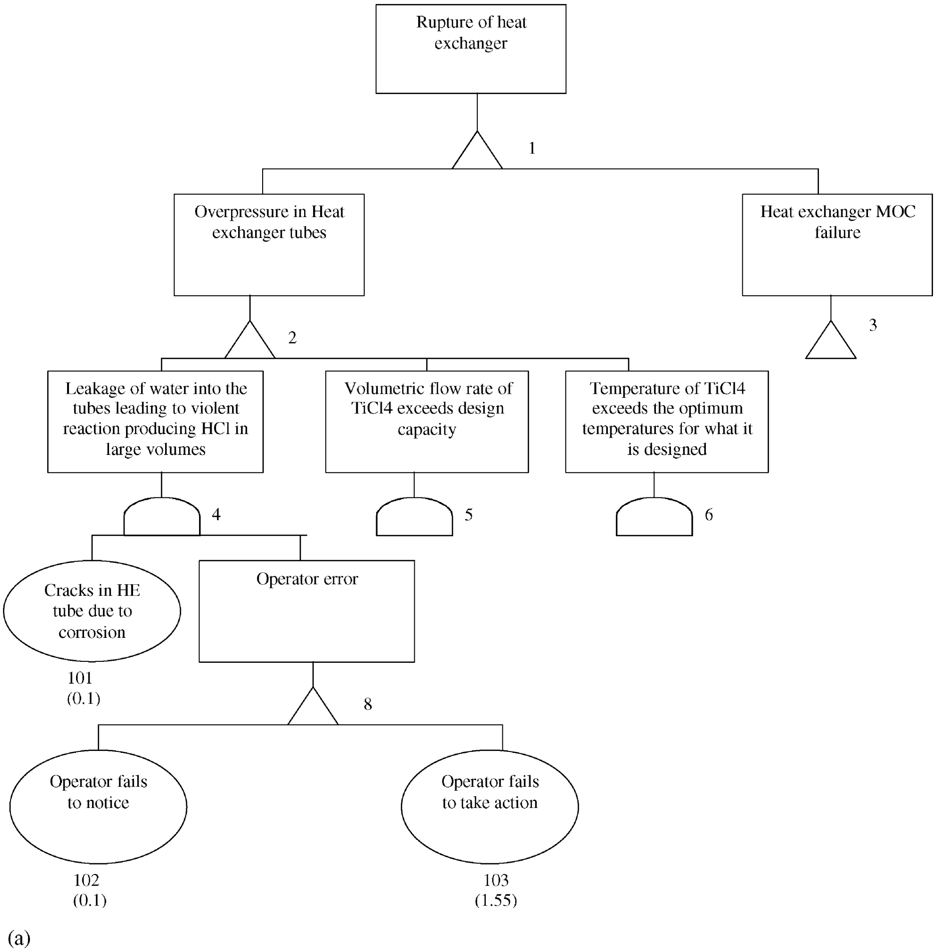


Fig. 3. Fault tree for rupture of HE.

Table 3
Sensitivity analysis results

Top event	Basic event	Recommendation	Top event occurrence	
			Before	After
Release of HCl due to spillage/leakage caused by rupture of storage tank	Electricity failure	Generator for auto take off	2.3E−02	2.96E−04
	Operator error	Operator training for normal and remedial measures	2.96E−04	1.06E−06
Rupture of HE	Upstream conditions not monitored/controlled	Operator training for monitoring upstream conditions	1.33E−02	4.31E−03
	Operator error in noticing the temperature	Alarm for high temperatures	4.31E−03	2.15E−03

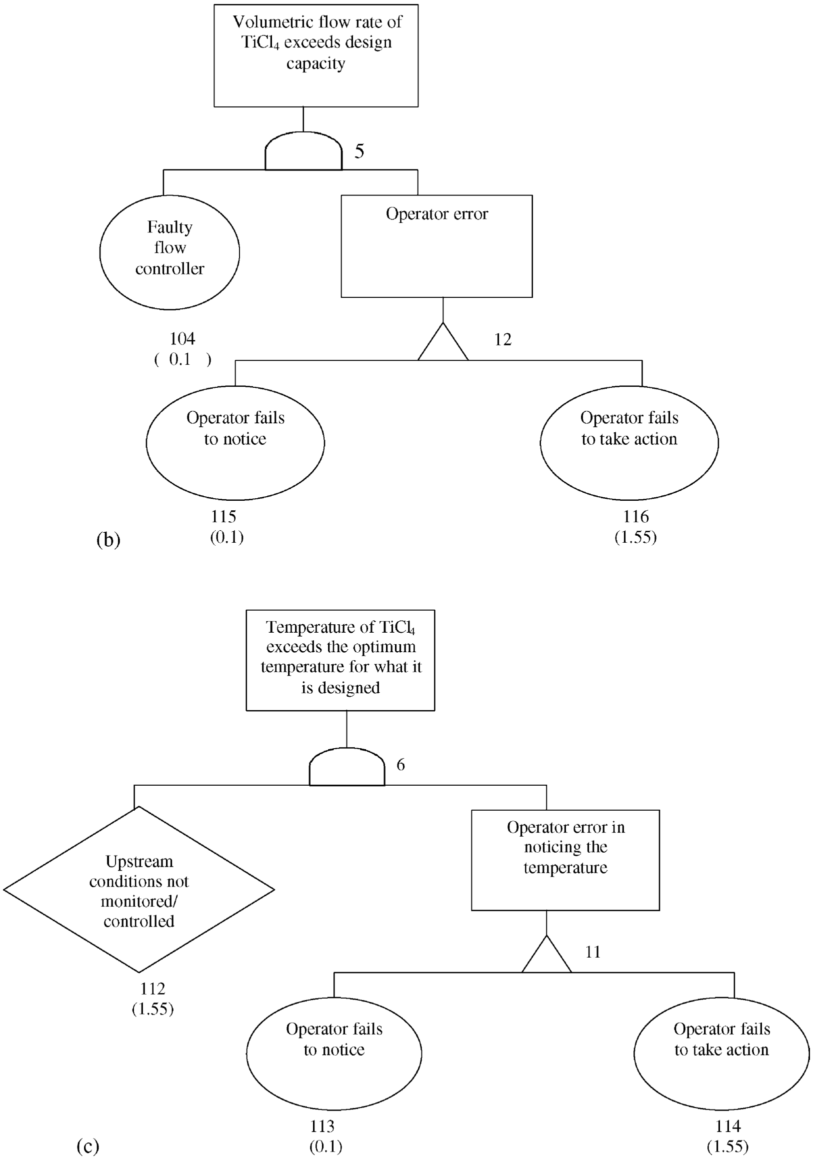


Fig. 3. (*Continued*)

1.5. Consequence analysis

1.5.1. Reaction with water

When $TiCl_4$ is spilled onto ground, a highly exothermic and violent reaction between $TiCl_4$ and water takes place. The products of the reaction are dependent on the availability

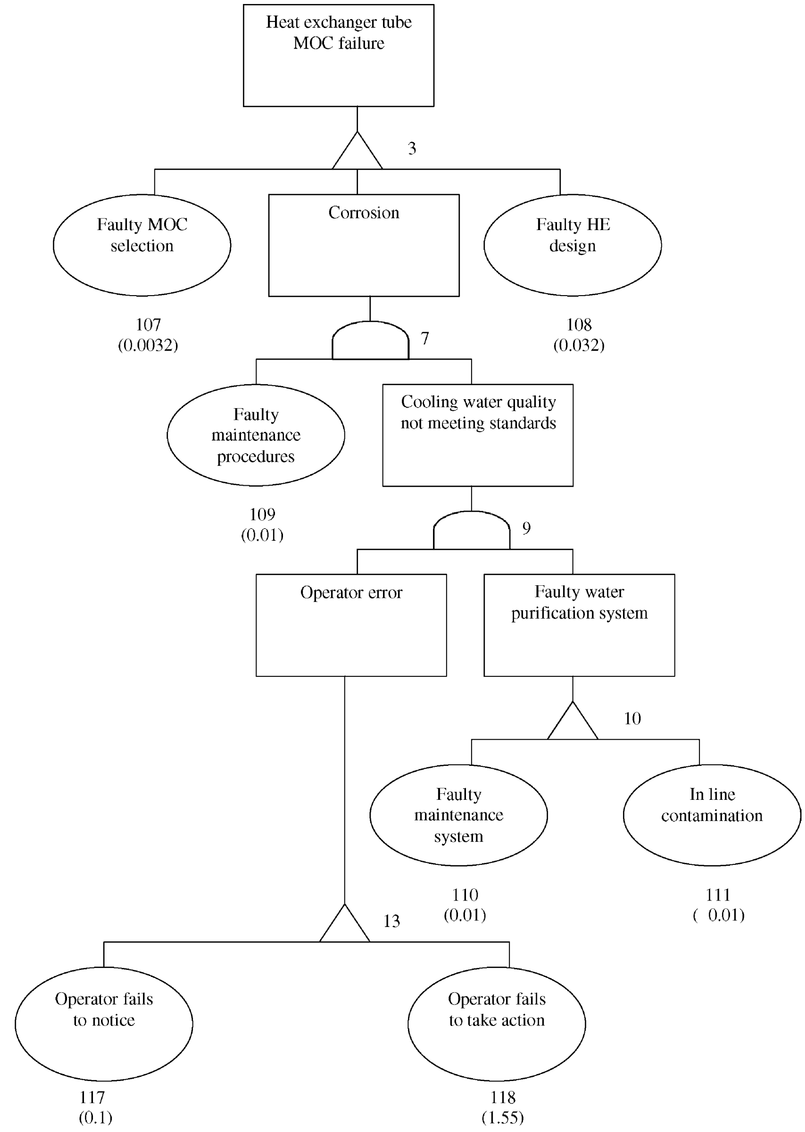


Fig. 3. (*Continued*).

of water. Overall the reaction can be represented by the following equations:

$$TiCl_4 + H_2O \rightarrow TiOCl_2 + 2HCl \quad \text{(when chloride is in excess)} \tag{1}$$

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl \quad \text{(when water is in excess)} \tag{2}$$

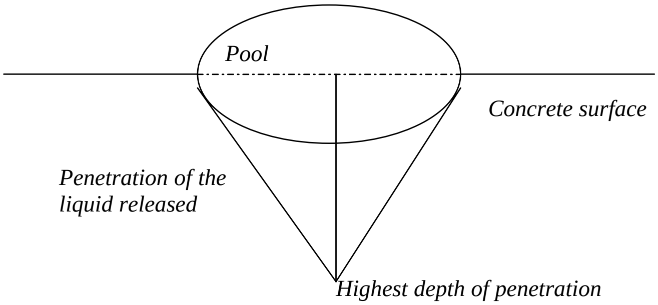


Fig. 4. Penetration of $TiCl_4$ in concrete.

The phase of the hydrochloric acid formed is strongly determined by the amount of water available for the reaction. If water is in excess a liquid aqueous solution of this acid is usually generated. If the $TiCl_4$ is in excess, the HCl will be directly evolved to the atmosphere.

In cases where $TiCl_4$ is stored, transported or used in their liquid form, e.g. in the storage section of the plant under study, a spill will create a liquid pool of $TiCl_4$ on the ground. There have been several attempts to model the behaviour of water reactive chemicals [23–26]. We have used a model similar to the one developed by Kapias et al. [26] for the present study.

However in the case of rupture of the HE, the HCl formed will be in its aqueous phase and a pool of HCl will be generated because of the availability of excess water. Both these scenarios have been considered below.

1.6. Model description

In the case of release of $TiCl_4$, a pool will be formed on the ground. However the penetration will not be uniform for the whole area of the pool. At the point of release, the penetration will be higher and at the edges of the pool, it will be the lowest. The volume of the substrate that has been permeated by the liquid will have the form of cone as shown in Fig. 4.

The pool spreads until it reaches a minimum layer thickness depending on the roughness of the substrate. The pool then shrinks as the volume decreases due to the evaporation and the depth then remains constant.

1.7. Pool radius calculations

It is assumed that out of the 25T of $TiCl_4$ stored in the Tank, 20T is released on rupture of the tank forming a pool confined to 1600 m^2. The pool depth has been calculated to be 0.07 m. Since we have considered an instantaneous release, the liquid is considered to be a cylinder that collapses and the equivalent pool radius has been calculated to be 22.6 m from the following equation:

$$R = \sqrt{\frac{V}{\pi h}} \tag{3}$$

where V is the volume of liquid spilled and h the pool depth.

1.8. Moisture available

The most important factor that governs the behaviour of the pool is the amount of water available for the reaction. The floor of the storage bay is made of concrete, so during spreading, the pool encounters free ground water, substrate water (including the water chemically bound in concrete) and also absorbs atmospheric moisture. After the pool has spread to the maximum extent, water is available only from the substrate and the atmosphere. The amount of water available from these sources is calculated below.

1.8.1. Free ground water, M_{gw} (kg)

The mass of water available from that present on the ground is [27,28]

$$M_{\mathrm{gw}} = 1000 \times \pi \times w_{\mathrm{g}} \times \rho \times R^2 \tag{4}$$

where R (m) is the equivalent radius of the pool, ρ (g/cc) the density and w_{g} the thickness of the water film on the ground. Assuming w_{g} to be 0.0005 m [26], M_{gw} has been calculated to be 802 kg.

1.8.2. Atmospheric water, M_{aw} (kg)

$TiCl_4$ has such a affinity for water that it can even take up water from the atmosphere. In the absence of any experimental data, a simple approximation for this flux is adapted. The moisture that enters the pool is calculated by integrating the atmospheric moisture content over the height range of z to H', where z and H' are the lower and upper height to which the atmospheric water can enter the pool. The value of H' depends on the pool size and for a water reactive chemical it is given by

$$H' = \tfrac{1}{30} R \tag{5}$$

By assuming $z = z_0$ (roughness length of the substrate), the volumetric flow rate per unit width between the height z_0 to H' will be given by

$$V_{\mathrm{a}} = \frac{U(z)}{\ln(Z/Z_0)} \left[H' \left(\ln\left(\frac{H'}{Z_0} \right) - 1 \right) + Z_0 \right] \tag{6}$$

Here $U(z)$ is the wind speed at a height z. Assuming $U(10) = 2$ m/s and an air density of 1.2 kg/m^3 the mass of moisture entering the pool in each time step (10 s) is given by

$$M_{\mathrm{aw}} = V_{\mathrm{a}} \times 1.2 \times f_{\mathrm{w}} \times \delta t \times 2R \tag{7}$$

where f_{w} (kg water/kg total air) is the mass mixing ratio of the water vapour in the air, δt the time step used in calculations and R the pool radius (22 m). The mass mixing ratio was read from the psycrometric charts [29] to be 0.020. At a height of 10 m and roughness length of 0.005 m, V_{a} was calculated to be 2.545×10^{-3} m^3/s. From Eq. (7) the M_{aw} has been calculated to be 722 kg.

1.8.3. Water from concrete, M_{c} (kg)

Total mass of water that the liquid encounters [26] in each time step (10 s) from concrete is

$$M_{\mathrm{c}} = \{(\tfrac{1}{3}\pi R^2 l)_{t_n} - (\tfrac{1}{3}\pi R^2 l)_{t_{n-1}}\} W_{\mathrm{cem}} + 0.2 M_{\mathrm{cemr}} \tag{8}$$

The various terms have been explained below.

W_{cem} is the amount of free water in the concrete, which depends heavily on factors such as the type of concrete, its compounds (cement and aggregates) and the environment it is exposed to. W_{cem} usually varies from 130 to 230 kg/m^3 [30,31]. For the present study, W_{cem} has been assumed to be 180 kg/m^3. M_{cemr} is the mass of cement encountered by the spilt liquid and it is calculated from the following equation:

$$M_{\mathrm{cemr}} = \{(\tfrac{1}{3}\pi R^2 l)_{t_n} - (\tfrac{1}{3}\pi R^2 l)_{t_{n-1}}\}C \qquad (9)$$

where $((1/3)\pi R^2 l)_{t_n}$ is the volume of cone at one time step and $((1/3)\pi R^2 l)_{t_{n-1}}$ the volume of cone at the previous time step. One meter is its depth (maximum penetration) and C (kg/m^3) the cement content in concrete which has been assumed to be 400 kg/m^3 [32]. The maximum penetration at each time step will be the cumulative penetration up to the time step plus the permeability multiplied by the time step:

$$l_{n+1} = l_n + k\,\delta t \qquad (10)$$

The permeability of $TiCl_4$ is given by

$$\begin{aligned} k_{\mathrm{TiCl_4}} &= (55.627\exp(-0.001852t) + 20.6315\exp(-0.000235t) + 1.3821) \\ &\quad \times 10^{-8}\,\frac{\nu_{\mathrm{H_2O}}}{\nu_{\mathrm{TiCl_4}}} \end{aligned} \qquad (11)$$

where ν is the fluids kinematic viscosity given by

$$\nu = \frac{\text{viscosity}}{\text{density}} \qquad (12)$$

From Eq. (9), M_{cemr} has been calculated to be 306 kg.

The total water $(M_{\mathrm{cemr}} + M_{\mathrm{aw}} + M_{\mathrm{gw}})$ was calculated to be 1830 or 101.6 kg mol H_2O.

1.8.4. Rupture of HE

In the HE, water (cooling medium) and $TiCl_4$ are circulated in the shell and tube, respectively. The flow rate of cooling water is 150 kg/h and the hold up for HE is 44 kg.

In case of a rupture in the HE, water will be in excess and the hydrochloric acid generated will be in its liquid phase.

1.9. Effects and damage calculations

Neutral dispersion model has been used to assess the effects of HCl dispersion into the surrounding atmosphere. TNO effects model and TNO yellow book [27] have been used to carry out the consequence analysis.

1.9.1. Dispersion calculations

1.9.1.1. $TiCl_4$ storage section. Assuming a time period of 30 min for the reaction of $TiCl_4$ released with the available water, the amount of HCl evolved was calculated to be 7421 kg. The data for the model is based on the wind speed data provided and the scenario has been estimated using a wind speed of 2 m/s and ambient temperature of 30 °C. Fig. 5 gives the

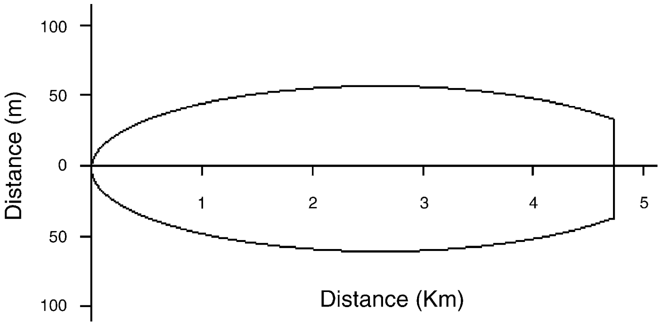


Fig. 5. IDLH contour for rupture of storage tank.

variation of concentration with the downwind distance up to IDLH (immediately dangerous to life and health) limits. The IDLH gives an estimate of the maximum concentration in air to which a healthy worker could be exposed for about 30 min without suffering permanent health effects. The population staying in a radial distance of 4725 along the wind direction needs to be alerted.

1.9.1.2. Rupture of HE. Assuming rupture of entire HE and a response time of 10 min, the amount of acid generated has been calculated to be 34 kg. Fig. 6 depicts the directional IDLH (145 mg/m^3) contour in case of rupture of HE. The scenario has been estimated at an ambient temperature of 30 °C and a wind speed of 0.2 m/s as the purification is carried out in an enclosed area. Generally, wind direction is least predictable at such low wind speed and so the footprint has been depicted in the form of a circle to indicate the uncertainty in direction.

1.9.2. Effect of seasonal variation

Based on the wind rose pattern supplied by the local meteorological department, the predominant wind direction during monsoon (17% of the time) is WNW so probability of

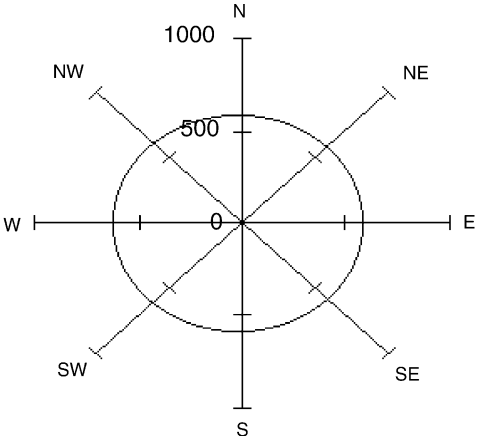


Fig. 6. IDLH contour for rupture of HE.

Table 4
Estimation of incident outcome and risk (season monsoon)[a]

Wind direction	Directional probability (%)	Population affected[b]	Incident outcome before recommendation	Risk and fatality before recommendation	Incident outcome after recommendation	Risk and fatality after recommendation
NNW	7	500	1.61E−03	8.05E−01	7.42E−08	3.71E−05
NW	14.5	500	3.34E−03	1.67E+00	1.54E−07	7.70E−05
WNW	17	800	3.91E−03	3.13E+00	1.8E−07	1.44E−04
W	11	1000	2.53E−03	2.53E+00	1.16E−07	1.16E−04
WSW	8	600	1.84E−03	1.10E+00	8.48E−08	5.09E−05
SW	12	600	2.76E−03	1.66E+00	1.27E−07	7.62E−05
SSW	9.5	600	2.19E−03	1.31E+00	1.01E−07	6.06E−05
S	1.5	200	3.45E−04	6.90E−02	1.59E−08	3.18E−06

[a] Before recommendation: incident frequency per year (2.30E−02). After recommendation: incident frequency per year (1.06E−06).

[b] Area considered for affected population = 5.1E+05 m^2.

HCl dispersing in this direction is maximum. During winters, the wind direction is reversed with the plume pointing towards ESE (47% of the time).

1.9.3. Incident outcome frequency calculations

The frequency of release of HCl due to storage tank rupture was found to be 2.3×10^{-2} per year. Based on this figure and the directional wind probability, the incident outcomes for both monsoon as well as winter season have been calculated as follows:

$$\text{Incident outcome} = \text{top event frequency} \times \text{probability of wind blowing in the direction} \tag{13}$$

The incident outcomes both before and after implementation of recommendation are summarised in Tables 4 and 5, respectively. After implementation of recommendations, the incident outcomes have been considerably reduced to 8.52E−07.

Table 5
Estimation of incident outcome (season winter)[a]

Wind direction	Directional probability (%)	Population affected[b]	Incident outcome before recommendation	Risk and fatality before recommendation	Incident outcome after recommendation	Risk and fatality after recommendation
N	2	500	4.60E−04	2.30E−01	2.12E−08	1.06E−05
NNE	2	500	4.60E−04	2.30E−01	2.12E−08	1.06E−05
NE	14	500	3.22E−03	1.61E+00	1.48E−07	7.40E−05
SE	47.5	600	1.09E−02	6.56E+00	5.035E−07	3.02E−04
SSE	1.5	600	3.45E−04	2.07E−01	1.59E−08	9.54E−06
S	8.5	200	1.96E−03	3.91E−01	9.01E−07	1.80E−04
SSW	3	600	6.90E−04	4.14E−01	3.18E−07	1.91E−04
WSW	2	600	4.60E−04	2.76E−01	2.12E−07	1.27E−04

[a] Before recommendation: incident frequency per year (2.30E−02). After recommendation: incident frequency per year (1.06E−06).

[b] Area considered for affected population = 5.1E+05 m^2.

The frequency of rupture of HE was found to be 0.0133 faults per year. Since the purification is carried out in an enclosed area, there will be no appreciable effect of seasonal variation in this case.

1.9.4. Damage calculations

1.9.4.1. $TiCl_4$ storage section. The effect calculations give the extent of the IDLH plume while the probability calculations give the directional probability of the incident outcome. Their damage potential is calculated based on the extent of IDLH plume and its superimposition on the layout of the plant and the surrounding areas. The population at risk has been estimated by considering the number of people living in the area delimited by the IDLH contour resulting from dispersion calculations. The extent of IDLH plume calculated from the model extends to about 4.7 km in the wind direction with a maximum width of 110 m, which corresponds to a exposed area of $\sim 0.519\,\text{km}^2$. Tables 4 and 5 give the area of exposure and population at risks during monsoon and winter season, respectively. If effective measures are instituted to evacuate the affected public within 30 min, then the damage will come down to the personnel present in the immediate vicinity within the plant. Assuming this figure to be 5, the damage will come down to 5 fatalities per incident. Onsite and offsite emergency plans need to be formulated and all district level agencies involved in emergency planning should be sensitised to the plans and participate in mock drills to aid evacuation.

1.9.4.2. Rupture of HE. From the IDLH plumes (Fig. 6) it can be concluded that the public present within 575 m radius of the HE would be affected. However since the operation is carried out in an enclosed area only plant personnel present in that room will be affected, which has been assumed to be two at any particular time. Personnel need to be provided with face masks throughout the operation. SOPs need to be framed to ensure that unprotected personnel do not enter the danger zone.

1.10. Risk assessment

From the probability calculations as well as the effect and damage calculations, the risk has been calculated as follows:

$$\begin{aligned}&\text{Risk (fatalities per year)}\\&\quad = \text{probability (events per year)} \times \text{damage (fatalities per event)}\end{aligned} \tag{14}$$

In the storage section the individual risk for both monsoon as well as winter season have been estimated and the results are summarised in Tables 4 and 5, respectively.

The total individual risk as seen from these tables is 12.3 fatalities per year during monsoon and 9.9 fatalities per year during winter. However after incorporation of the recommendations suggested the fatalities will be brought down to 5.65E−4 and 9.05E−4, respectively, for monsoon and winter season, respectively. According to Table 6, the frequency of 2.3E−02 (before implementing recommendation) falls under “Frequent” category, while the damage falls under “Catastrophic” category. Thus the risk falls under “A” category—Unacceptable. After incorporating the recommendation the frequency comes down to 1.06E−6 which falls under the “Improbable” category, bringing down the risk to

Table 6
Risk assessment matrix

Frequency of occurrence		Hazard category[a]			
		Catastrophic, >100	Critical, 10–100	Marginal, 1–10	Negligible, <1
Frequent	0.01	A	A	A	C
Probable	0.001	A	A	B	C
Occasional	0.0001	A	B	B	D
Remote	E−4	B	B	C	D
Improbable	E−6	C	C	C	D

[a] A: unacceptable; B: undesirable (management decision); C: acceptable with review; D: acceptable without review.

"C" category—Acceptable with review. After implementation of protective measures, i.e. evacuation and assuming only five plant personnel present at the site the damage comes "Marginal" category.

In case of rupture of HE the area exposed is likely to be within 575 m radius of the source. However, due to enclosed nature of the process area, the actual area of exposure would be much lower. Further there is provision for ventilation of the building, which would partially handle the HCl vapour generated. It is therefore assumed that the fatalities would be restricted to the personnel within the building. The individual risk has been estimated to be 0.0665 fatalities per year assuming five persons to be present within the building at the time of incidence. According to Table 6, the frequency of 0.0133 faults per year (before implementation of recommendations), falls under the "frequent" category while the damage comes under the "Marginal" category. Thus the risk comes under "A" category—Unacceptable. After incorporating the recommendations the frequency comes down to 0.0043 faults per year, and the risk comes down to 0.0215 faults per year.

2. Conclusion

FETI and HAZOP studies of titanium production plant identified the storage and purification sections of the plant to be the most hazardous sections. Both these sections handle titanium tetrachloride in large quantities. Titanium tetrachloride is a water reactive chemical which generates HCl fumes instantaneously in presence of moisture. Hence spillage of titanium tetrachloride was considered as the top event for the fault tree analysis. The basic event responsible for the top event occurrence were identified using the probabilistic fault tree analysis technique. Protective and preventive measures were recommended to reduce the probability of top event occurrence and hence the associated risks. The damage studies involved dispersion behaviour of the evolved plume for probable scenarios. The results reveal that in the worst case scenario (monsoon season), the threat zone extends to an inhabited area of 0.5 km^2. Hence appropriate offsite and onsite emergency plans need to be formulated to aid evacuation in the event of titanium tetrachloride release.

A comprehensive risk assessment of plants which involve storage and handling of titanium tetrachloride and other water reactive chemicals is recommended as they provide crucial inputs for risk management decisions.

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